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New Volumetric Method for the Determination of Copper

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A New Volumetric Method for the Determination of Copper

...BY...

ARTHUR RUSSELL JOHNSTON

THESIS

FOR THE DEGREE OF

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

A. R. Johnston

ENTITLED A New Volumetric Method for

The Determination of Copper

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE

OF Bachelor of Science in Chemistry

A. V. Parr

HEAD OF DEPARTMENT OF Applied Chemistry

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A New Volumetric Method for the Determination of Copper.

From the standpoint of the analytical chemist there is as yet no trustworthy and at the same time rapid method for the determination of copper in ores and mattes. The methods already in use are long and tedious and still are not over accurate. At present there are two methods which are universally used and are considered to be trustworthy. Of the two methods one is known as the cyanide method and the other the iodide method.

The cyanide method depends upon the fact that the addition of potassium cyanide to an ammoniacal copper solution affords a colorless solution containing cuprous ammonium

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cyanide and other compounds. The results are influenced by the proportions of copper, of free ammonium, and of ammonium salts present, by the bulk of solution, and by the presence of many of the metals other than copper. Thus one can see that it must be somewhat difficult to always have the conditions the same. Then again this method requires that the copper should be in solution by itself, other metals influencing the result. This is difficult and requires considerable time. At the end where the decolorization of the solution takes place by adding the cyanide solution the work must be done very slowly or otherwise one is very apt to overrun the end reaction. Taking all the conditions and precautions necessary in this method into account one is

able to understand the difficulty of working with such a method.

The iodide method depends upon the reaction: —

$$2\,Cu(C_2H_3O_2)_2 + 4\,KI = Cu_2I_2 + I_2 + 4\,KC_2H_3O_2$$

Cuprous iodide precipitates and a proportional amount of iodine is set free, which may be determined by titration with sodium thiosulphate.

Salts of iron, lead, bismuth, arsenic, antimony and perhaps others influence the reaction so that in this case as in the other it is necessary to obtain the copper free. Free mineral acids interfere so that it is necessary to boil off all such. In the end reaction here one is apt to be deceived because the cuprous iodide in itself possesses a faint pinkish tinge. There is scarcely any choice between the two methods

In the last few years there has been two other methods presented.

The first presented by W. C. Ganiques in 1897. This consists in precipitating the copper as cuprous sulphocyanide according to Rivot. That is the solution is evaporated with as little sulphuric acid as possible to expel any volatile acids, warmed gently after dilution and sulphurous acid added until its presence is plainly apparent by odor. The precipitation being now made with an alkali thiocyanate. When the liquid settles perfectly clear which is promoted by further warming, filter and wash well with water.

The filter and contents is transferred back to the beaker in which the precipitation was made, boiled with a measured

excess of standard caustic alkali then cooled and diluted to a convenient bulk. After passing through a dry filter, a part of the filtrate is taken and titrated to neutrality with standard acid and methyl orange. The rationale of the process is that caustic alkali converts thiocyanate into cuprous hydroxide and alkali thiocyanate, the later body being neutral to methyl orange.

The reaction:—

$$2CuCNS + 2NaOH = Cu_2(OH)_2 + 2NaCNS.$$

The other method was presented by Richard K. Meade in 1898. The method consists in precipitating the copper as cuprous sulphocyanate the same as the former then treated with caustic alkali. But in this case instead of using a standard solution of caustic and titrating the excess the author makes use of the re-

any which requires considerable time. While my work lies along the same line I have endeavored to obtain a method so that only one precipitation and washing will be necessary. For this work I made up a solution of copper sulphate and standardized it electrolytically.

1 c.c. = .0666 Cu.

My method of procedure consisted in taking aliquot parts of the standard copper solution heating to boiling, making slightly acid with sulphuric acid. To the boiling solution add 10 c.c. of sodium acid sulphite solution, to keep the precipitate in the form of the cuprous salt, then add 10 c.c. of ammonium sulphocyanide solution. This precipitates the copper as cuprous sulphocyanide. Digesting a few minutes to make

sure of entire precipitation then filter through an asbestos filter. Wash with hot water till the filtrate will no longer reduce a permanganate solution. This washing being for the entire removal of bisulphite and the excess of ammonium sulphocyanide. After washing the precipitate is removed with the asbestos and transferred to a No. 3 or 4 beaker, (the same beaker the precipitation was made in). The filter funnel is rinsed with NH_4OH to make sure of the entire removal of $Cu\,CNS$ and run into the beaker containing the precipitate. Enough more ammonia is added to entirely dissolve the precipitate. Now we have an ammoniacal solution of cuprous sulphocyanide. This is treated with two or three drops of freshly

prepared solution of sodium peroxide and digested for twenty minutes without boiling. (The idea in using the sodium peroxide being to find a means of oxidizing the copper and still not break down the thiocyanate.) The digestion being for the purpose of entirely eliminating any trace of the excess of sodium peroxide and complete oxidization of the copper. After digestion the solution is acidified with H_2SO_4 and then titrated with permanganate.

The permanganate solution in use being standardized. The permanganate has the factor

1 c.c. = .006802 8 Fe.

according to the following two equations:—

(1) $6\ K_2Mn_2O_8 + 10\ HCNS + 6\ H_2SO_4 =$
$6\ K_2SO_4 + 12\ MnSO_4 + 10\ HCN + 8\ H_2O.$

(2) $K_2Mn_2O_8 + 10\ FeSO_4 + 8\ H_2SO_4 =$
$K_2SO_4 + 2\ MnSO_4 + 5\ Fe_2(SO_4)_3 + 8\ H_2O$

We have since 10 HCN's = 10 Cu.

$56 \times 10 \times 6 : 63 \times 10 :: .0068028 : X$

X = grams of Copper represented by 1 c.c. of permanganate = .001275 grams Cu.

Following the method as outlined above I give below the results obtained with three trials.

(1.) Taking 10 c.c. of the copper sulphate solution obtained.

.0648 Cu. should be .0661 Cu.

(2.) Same as above obtained

.0636 Cu should be .0661 Cu.

(3.) Obtained

.0637 Cu should be .0661 Cu.

I made several other attempts with the Na_2O_2 but always failed to obtain concordant results. Evidently in the use of sodium peroxide some of the sulphocyanate is broken up as shown by the low reading obtained.

Being unable to accomplish

the desired result by the use of sodium peroxide I turned to another method of oxidization. Precipitating and washing in the same manner I transfered to the original beaker, dissolved in ammonia then instead of using any chemicals for the oxidization I digested in the air for twenty to thirty minutes. After digesting made acid as before and titrated.

Following are the results of my experiment:—

I. 10 c.c. of $CuSO_4$ sol. taken

Titre 50.5

50.5 X .001275 = .064412 grams Cu.

1 c.c. $CuSO_4$ sol = .006441 grams Cu.

Should be .00661 " " .

II. 10 c.c. of $CuSO_4$ sol.

Titre 50.6

50.6 X .001275 = .064604 gms. Cu.

1 c.c. $CuSO_4$ sol. = .006604 " "

Should be .00661 " " .

III. 10 c.c. $CuSO_4$ sol. taken.

Titre 50.75

50.75 x .001275 = .06473 gms. Cu.

1 c.c. $CuSO_4$ sol = .006473 " "

Should be .00661 " "

The latter two stood over night before filtering.

IV.

Took 25 c.c. of the copper sulphate solution precipitated in the same way. After oxidizing the cuprous sulphocyanide and converting it into a cupric soluble compound by heating and stirring and making acid the asbestos was filtered off and the filtrate made up to 500 c.c. The asbestos was removed from the funnel and treated with ammonia heated for some time when a blue tint appeared. After standing for a few minutes it was made acid and titrated.

Titre 1.9 c.c. permanganate sol. This I added to the titrations

made on aliquot parts of the 500 c.c. filtrate.

(a) 50 c.c. of the 500 c.c.

Took 12.35 c.c.

$(12.35 \times 10) + 1.9 = 125.4$ c.c. for 25 c.c. $CuSO_4$ sol.

$125.4 \times .001275 = .159947$ gms. Cu.

1 c.c. $CuSO_4$ sol = .00639 " "

Should be .00661 " "

This seems to show that not all the CuCNS had been oxidized and dissolved.

(b.) Took 50 c.c. of the remainder made alkaline with NH_4OH and heated for 10 or 15 minutes with frequent stirring then acidulated with dilute H_2SO_4 and titrated.

Took 12.5

$12.5 \times 10 = 125$

$125 + 1.9 = 126.9$ c.c. for 25 c.c. $CuSO_4$ sol.

$126.9 \times .001275 = .1608669$ gms. Cu.

1 c.c. $CuSO_4$ = .006434 " "

Should be .00661 " "

(c.) Same as (b) but allowed the alkaline solution to

stand at 100° C for one hour before making acid and titrating.

Titre 12.55 c.c.

12.55 × 10 = 125.5

125.5 + 1.9 = 127.4 c.c.

127.4 × .001275 = .161498 gms Cu.

1 c.c. = .00646 " "

Should be .00661 " "

V. Took 50 c.c. of the $CuSO_4$ solution same as III but heated with NH_4OH for 3 or 4 hours before making acid and filtering off the asbestos. Diluted the filtrate to 500 c.c. Here the oxidation was aided materially by passing air through the alkaline solution.

(a) 50 c.c. of the 500 c.c.

Titre 25.3 c.c.

25.3 × 10 × .001275 = .32270 Cu.

.32270 ÷ 50 = .006454 gms. Cu.

1 c.c. $CuSO_4$ = .006454 gms Cu.

Should be .00661 " "

(b) Same as (a)

Titre 25.35

25.35 X 10 X .001275 = .32333 gms Cu.

1 c.c. $CuSO_4$ = .00676 " "

Should be .0066 " "

VI. Repeated II but added H_2O_2 to the alkaline solution after going through the subsequent work much of the H_2S was found to have been destroyed as the titration came out very low.

III Again took 50 c.c. of $CuSO_4$ solution. Precipitated as usual. After filtering and washing off the precipitate treated hot dil. HNO_3 with some $(NH_4)_2SO_4$ present on the precipitate and drew a current of air through by means of filter pump. This was continued adding small amounts of ammonia for several minutes.

made filtrate up to 500 c.c. and transferred the asbestos with the remaining precipitate to the beaker added NH_4OH and heated on a hot plate. After about 15 minutes made acid with dilute H_2SO_4 (40 c.c.) and titrated.

Titre 16.1 c.c.

Taking aliquot parts of the 500 c.c. filtrate & now titrated them.

(a.) 50 c.c. of 500 c.c. filtrate. added 50 c.c. dilute H_2SO_4 warmed and titrated

Titre 23.2 and 23.1

(b.) 50 c.c. of the remainder heated the asbestos shut for one hour and titrated after adding 50 c.c. of dilute H_2SO_4.

Titre 23.2 and 23.

For 500 c.c. we have:—

$(23.2 \times 10) + 16.1 = 248.1$ c.c.

$248.1 \times .001275 = .31632$ grm Cu.

1 c.c. $CuSO_4$ = .006326 " "

Should be .006361 " "

After all two years of trying to oxidize in the air I am forced to the conclusion that all of the copper is incapable of oxidization by action of the air alone.

Unable to obtain satisfactory results by simply oxidizing in the air the following experiments are made with different oxidizing agents in an effort to find one if possible which will completely oxidize the Cu and still leave the Thiocyanate undisturbed.

I.) 10 c.c. of $CuSO_4$ solution taken. The precipitate of Cu CNS treated with dil. HNO_3 did not change with the

addition of NH_4OH until it was strongly alkaline and after standing on an asbestos sheet for 1 to 1½ hours.

Tube 47.8 c.c.

Should be 50.5 c.c.

The blue color did not seem to come more readily.

II. Same as I but added NH_4OH and Na_2HPO_4 to the $Cu\,CNS$ precipitate. Heated on asbestos sheet for 1 hour.

Tube 49 c.c.

Should be 50.5 c.c.

Very unsatisfactory end reaction.

Oxidation of the Cu does not seem to take place any more readily.

III. Same as I. Before making alkaline the $Cu\,CNS$ precipitate was treated with Bromine water. No change. Heated for some time. No change. Added NH_4OH and heated

for 1 hour.

Titre 45.2 c.c.

Should be 50.5 c.c.

II. Same as I. but imediately added NH_4OH to the $CuCNS$ precipitate and heated as usual.

Titre 49.2 c.c.

Should be 50.5 c.c.

III. Took 10 c.c. of the $CuSO_4$ solution precipitated as usual, filtered and washed. Returned precipitate and asbestos to beaker and added $NaOH$. The $Cu_2(OH)_2$ precipitated. On adding $(NH_4)_2SO_4$ and NH_4OH to this it readily dissolved. In this case however I filtered off the hydroxide washed well and titrated the filtrate after adding dilute H_2SO_4.

Titre 51.7 c.c. Should be 50.5 c.c. This high value probably due to the fact that some of the cuprous copper passed

through the filter and
washed. The asbestos with
the impure copper precipitate
was treated with NH_4OH and
$(NH_4)_2SO_4$ and heated until
dissolved. Then made acid
and titrated.

Time about 50 c.c.

Thus far the results obtained
in some cases duplicating
very well all appear to be
a final result somewhat
lower than the electrolytic re-
sult for the $CuSO_4$ solution.
For the sake of discovering
whether the trouble was in
the precipitation of the
$CuCNS$ I took a measured
volume of the $CuSO_4$
solution precipitated as
usual, filtered and washed
thoroughly. The precipitate
& filter was put in the assay
and over N_2SO_4 and dissolved
the dry salt. & found the
result to be almost exactly

What the electrolytic action was. Thus knowing that the iron was not in the precipitation we must look elsewhere for it. It is the next step in the solution of the silver.

I next tried some experiments with cuprous oxide as an oxidizing medium. This is the same as the two methods of Wade and Carnegie but instead of boiling the $Cu_2(OH)_2$ I shook with permanganate in the alkali medium and then made acid with dilute H_2SO_4 and ammonium sulphate in an acid medium.

Reaction:—

$$7K_2Mn_2O_8 + 10Cu_2H_2S + 21H_2SO_4 = 7K_2SO_4 + 17MnSO_4 + 18H_2O + 10CuSO_4 + 10H_2O.$$

∴ the equation reads:

630 : 56 × 10 × 7 :: X : Factor of permanganate.

In this case the Fe factor = .0571

then X = .00917 the value of permanganate.

I. Took 5 c.c. of the $CuSO_4$ solution precipitated as usual, boiled and rinsed. Washed precipitate into the beaker the precipitation was made in, added 5 c.c. of 10% solution of caustic soda. Heated on water bath for a few minutes, added dil. N_2SO_4 until acid. Then titrated

Titre 35.9 c.c.

$35.9 \times .008917 = .032923$ Cu.

1 c.c. $CuSO_4$ sol = .00658 gm Cu.

Should be .0066 " "

II. Took 50 c.c. in the same manner. To the alkaline solution added 10 c.c. of permanganate solution made acid with dil. N_2SO_4 filtered off the asbestos and washed on the funnel once. Transferred to beaker made acid with dil. N_2SO_4 and titrated

Titre 40.25 c.c.

Made up filtrate to 500 c.c. and titrated aliquot parts.

50 c.c. titre 21.55.

for sample we have

35.5.75 c.c. permanganate

35.5.75 × .008917 = .326222 gms. Cu.

1 c.c. $CuSO_4$ = .00652 " "

Should be .00661 " "

III. Took 5 c.c. $CuSO_4$ solution same as I but when adding permanganate to the alkaline solution containing the $Cu_2(CN)_2$ it was diluted and after adding dilute H_2SO_4 heated on water bath and finished titration.

Titre 35.2 c.c.

35.2 × .008917 = .032478 gms Cu.

1 c.c. $CuSO_4$ = .00649 " "

Should be .00661 " "

Working along the same line as in II several precipitations and titrations were made with the following results.

5 cc. Cu SO4	taken	Titre 10.9	.00649 gms Cu.
"	"	" 11.1	.00661 " "
"	"	" 11.	.00653 " "
10 cc. Cu SO4	"	" 21.9	.00652 " "
		Mean	.00658 " "
50 "	"	" 117.8	.00701 " "
25 "	"	" 60.8	.0072 " "
20 "	"	" 42.9	.00640 " "

More results with a different ammoniacal sol.

Taken.	Titre.	Value.
5 c.c.	8.9	.00644
5 "	9.1	.00666
5 "	9	.00659
5 "	9	.00659
5 "	9.05	.00661
10 "	18.6	.00678
10 "	18.6	.00678
15 "	27.35	.00664
15 "	27.	.00657
10 "	19.35	.00704

cyanide iodide ammoniacal sol.

10 "	71.5	.00664
10 "	71.5	.00664
20 "	143	.00664
20 "	146	.00671

Trying to find cause for variation several tests were made. The green permanganate proved at the end of the titration was thought owing to cause it but taking a standard solution of $KMnO_4$ 0.1 S making strongly alkaline and then adding 2 or 3 c.c. of permanganate heating on water bath and allowing it stand in the air for an hour it still titrated correct.

Thus:-

10 c.c. $KMnO_4$ 0.1 S + 2 c.c. $NaOH$ + 2.5 c.c. of $MnSO_4$.

Heated on hot plate for a few minutes. Cooled diluted, acidulated with dil. H_2SO_4 and titrated hot with

Tire 6.05 c.c.

Should be 6. c.c.

Two other samples tested in the same manner gave

correct readings.

Another sample was taken and titrated in the same manner then allowed to stand for 1 hour.

Titre 6.1 c.c.

Should be 6 "

This data proves that there was very little chance for error at this point.

I ran a few tests using different strength solutions of caustic soda and also tried warming the caustic solution before adding the permanganate.

I found that warming the caustic facilitated the oxidation while it did not seem to vary the readings.

F. (a) 5 c.c. $CuSO_4$ solution.

Precipitated as usual.

Treated the precipitate with 10 c.c. 5% caustic solution and warmed.

Titre 9.7 c.c.

(c) Another sample treated in the same way.

Titre 9.2 c.c.

II. (a) 5 c.c. $CuSO_4$ solution. Precipitated as usual. Treated with 6 c.c. 20% caustic solution and warmed.

Titre 9.85 c.c.

(b) Same as (a)

Titre 10 c.c.

(c) Same as (a)

Titre 9.4 c.c.

Still unable to obtain satisfactory results I ran a few tests using caustic potash instead of caustic soda.

I. (a) 5 c.c. $CuSO_4$ solution. Precipitated as usual. Treated with 5 c.c. 10% caustic potash solution in cold.

Titre 31.4.

(b) Same as (a)

Titre 34.3

(c) Same as (a)

Titre 31.4

From the above results one can see that sometimes my results duplicate and then again they have a wide variation. I again go back to my original method of precipitation and try to find the cause. Without any $CuSO_4$ solution I heat dilute H_2SO_4 with $Na_2S_2O_3$ and NH_4CNS after heating for a few minutes a precipitate of sulphur appears. Thus I find a chance for error. Thinking that perhaps the $Na_2S_2O_3$ that I am using is not pure but might contain some $Na_2S_2O_3$. I make up a solution of HCl by heating $CaCl_2$ with concentrated H_2SO_4. Now using this solution and proceeding in the same manner as with

the Na_2SO_3. & find the sulphur is still precipitated. This fact goes to show that one is unable to obtain accurate results with any present method of procedure. The problem now is how to get the precipitate of $CdCN_2S$ with out precipitating any sulphur.
To overcome this I used by different acid medium for the precipitation.
First I took HCl and ran a blank the same as above. In this case as with H_2SO_4 the sulphur is thrown down. Next I tried HNO_3 and by using this as the acid medium for precipitation the sulphur does not separate.
The high readings that I have obtained were evidently due to the separation of the sulphur while the

low readings is attributed to the incomplete precipitation of the copper.

Now as I have a medium in which I think all things are overcome I will again work with the copper.

I. (a) 5 c.c. $CuSO_4$ diluted to 100 c.c. acidulated with HNO_3 Then precipitated in usual fashion filtered and washed.

Titre 30.7 c.c. = .00620 gms Cu

(b.) Same as (a)

Titre 30.8 c.c. = .00622 gms Cu

II. (a) 10 c.c. $CuSO_4$ solution Method & procedure same as in I.

Titre 63.8 c.c. = .00644 gms Cu.

(b.) Same as (a)

Titre 63.5 c.c. = .00641 gms Cu

(c.) Same as (a)

Titre 63.3 c.c. = .00639 gms Cu.

(d.) Same as (a)

Titre 63.6 c.c. = .00642 gms Cu.

These results duplicating so well it begins to look

promising but upon
figuring them up I find
that they are all low.
This I found to be due
to incomplete digesting on
the last titrate and consequently
the Cu was not all precipitated.
From the following tests which
I made very carefully I
have some good results.

I (a) 5 c.c. $CuSO_4$ solution.
Diluted to 100 c.c. and added
5 c.c. $+NO_3$ sp. gr. 1.135. A small
amount of NH_4CNS solution.
Boiled for 15 minutes added
and titrated thus titrated
using 5 c.c. 20% caustic sol.
and heating.

Tube 32.8 c.c.
1 c.c. $CuSO_4$ = .00663 Cu.
Should be .00661 "

(b) Same as (a)
Tube 32.6 c.c.
1 c.c. $CuSO_4$ = .00659 gms Cu.
Should be .00661 " "

(c) Same as (a)

Titre 32.8 c.c.

1 c.c. $CuSO_4$ = .00663 gms Cu.

Should be .0066 " "

(d) Same as (a)

Titre 32.5 c.c.

1 c.c. $CuSO_4$ = .00657 gms Cu.

Should be .0066 " "

(e) Same as (a)

Titre 32.7 c.c.

1 c.c. $CuSO_4$ = .00660 gms Cu.

Should be .0066 " " .

II. (a) 10 c.c. $CuSO_4$ solution

Treated same as I.

Titre 65.4 c.c.

1 c.c. $CuSO_4$ = .00660 gms. Cu.

Should be .0066 " "

(b) Same as (a)

Titre 65.6 c.c.

1 c.c. $CuSO_4$ = .00663 gms Cu.

Should be .0066 " "

III. 20 c.c. $CuSO_4$ solution

Same treatment as above.

Titre 130.6 c.c.

1 c.c. $CuSO_4$ = .00659 gms Cu.

Should be .0066 " "

II. 40 c.c. $CuSO_4$ solution.
Same treatment as above.
Tube 372.
1 c.c. $CuSO_4$ = .00660 gms. Cu.
Should be .0066 " " .
By the use of the nitric acid instead of sulphuric acid it suggests a very rapid method for running Copper matte.
Method of procedure being to dissolve the matte in nitric acid dilute to amount sufficient to give the nitric acid about the strength used in precipitating the copper. Take aliquot parts of this solution precipitate and titrate.
Following this method I ran a matte obtaining very nearly the same result as was obtained electrolytically.
1 gm. of matte dissolved in 50 c.c. of HNO_3 1.135 sp. gr.

diluted to 500 cc.

100 cc. of this 500 cc. precipitated as usual with NH4CNS and sulphurous acid, filtered, washed and titrated.

Tube 135 cc.

135 x .00072 Cu. factor of NH4VO4 = .0972 gms Cu.

.0972 x 5 = .4860 gms Cu. or 48.6 %

Electrolytic factor being 48.8 %.

More work along this line developed several very interesting facts.

If for instance one has a solution of over 2% nitric acid, the nitric acid will react with the cyanate and the entire breaking down of the sulphocyanate will take place. Hydrocyanic acid being formed in the reaction. Any amount of acid below 2% seems to work all

right. If a large excess of sulphite is added the copper may be precipitated clear from a neutral solution. Enough acid evidently being formed from the solution of the sulphite. Another point is the use of the ammonium sulphocyanate in the precipitation of the copper. An excess of the cyanate will dissolve the precipitate of CuCNS to some extent so it is necessary to use the least possible quantity in the precipitation. 1 cc. of a 5% solution being plenty to precipitate 50 mg. of copper. An excess of acid while it will not act upon the CuCNS after precipitation, prevents the precipitation.

In washing the precipitate it is necessary to wash till the filtrate will no

longer reduce a permanganate solution.

In the final titration in the acid solution if the permanganate turns brown, it is a sign of too small an amount of sulphuric acid. Concentrated acid should never be used.

Work upon
Sulphocyanate solutions.

All of the foregoing work depends upon the constancy of titration of the cyanate & the permanganate. In order to secure this point I made up three solutions of ammonium sulphocyanate. One of these I made an acid solution. Another I made an ammoniacal solution and the third was a neutral solution. These solutions were made up about the first of October, 1899. At different intervals during the school year I have made titrations upon them. These titrations proved the constancy and non-deterioration

upon standing. The results indicate that they are very stable and a standard solution of such will keep indefinitely. Thus we have a method for standardizing permanganate solutions. By keeping a standard solution of ammonium sulphocyanate always present we may standardize a permanganate solution in a very few minutes. Following are the results obtained in terms of the Fe value per cc. of the sulphocyanate solution as titrated at different times during the year. Results with the permanganate solution.

1 cc. of $KMnO_4$ = .0062 gm Fe.

Now having the value $KMnO_4$ always I will insert the

value of it when it changes.

1898 Date	Titre	Unit taken	Fe value.
10/10	19.7	10 c.c.	.012214
10/27	19.8	"	.012276
11/7	19.8	"	.012276
1 c.c. $KMnO_4$ = .0061 Fe.			
11/23	20	10 c.c.	.01220
1900 1/8	20	"	.01220
1 c.c. $KMnO_4$ = .0185 Fe			
1/9	6.7	10 c.c.	.012210
1 c.c. $KMnO_4$ = .02229 Fe			
3/2	5.5	10 c.c.	.012250
3/19	5.6	"	.012432

The high results were due to having such a strong permanganate solution.

Results with the acid titrated.

Date	Unit taken	Titre	Fe value.
1899 10/10	10 c.c.	21.4	.01326
10/27	"	21.6	.01339
11/7	"	21.7	.01345
11/23	"	21.9	.01335
1900 1/8	"	21.9	.01335
1/9	"	7.2	.01332
3/2	"	5.9	.01315
3/19	"	6	.01337

The seemingly increasing strength of the cuprocyanide solutions is due to the deterioration of the ferrocyanide. Result with the normal solution.

Date		Unit taken	Title	Factor.
1899	10/6	10 cc.	24.7	.015 31
	10/27	"	24.6	.015 25
	11/7	"	24.8	.015 37
	11/23	"	25	.015 25
1900	1/9	"	25.1	.015 31
	1/9	"	8.3	.015 35
	3/2	"	6.8	.015 15
	3/19	"	6.9	.015 38

I ran a number of tests to find the action of different salts acids, alkalies when in solution in quantity on the cuprocyanide solution.

Test with an excess of Na_2CO_3.

I. (a) Took 10 cc. of NH_4CNS solution added a large

excess of Na_2CO_3 heated made acid with dilute H_2SO_4 and titrated.

Titre 7.3 c.c.

Should be 7.3 c.c.

(b.) Same as (a.)

Titre 7.4 c.c.

Should be 7.3 c.c.

(c) Same as (a)

Titre 7.35 c.c.

Should be 7.3 c.c.

Thus an excess of Na_2CO_3 seems to have no detrimental effect on the titration.

II. (a) Took 10 c.c. of N/10 $(NH_4)_2S$ solution made it strongly ammoniacal heated then made acid with dilute H_2SO_4 and titrated.

Titre 7.4 c.c.

Should be 7.3 c.c.

(b.) Same as (a)

Titre 7.3 Should be 7.3 c.c.

(c.) Same as (a)

Titre 7.25 c.c.

Should be 7.3 c.c.

Thus ammonia does not effect it.

III. (a) Took sample in same way and boiled with Na_2CO_3 for 20 minutes then made acid and titrated.

Titre 5.8 c.c.

Should be 7.3 c.c.

(b) Same as (a)

Titre 5.9 c.c.

Should be 7.3 c.c.

(c) Same as (a)

Titre 5.2 c.c.

Should be 7.3 c.c.

Boiling with Na_2CO_3 makes up the cyanate.

III. Tried making acid with conc. H_2SO_4 with unsatisfactory results.

(a) 10 c.c. N/4 CNS Titre 6.8 should be 7.3

(b) " " " 7.3 " "

(c) " " " 5.5 " "

(d) " " " 7 " "

The conc. H_2SO_4 oxidising reacts with the cyanate breaking it down.

II. Boiling with an excess of NH_4OH

(a) 10 cc. NH_4CNS Tube 7.3 Standard 7.3
(b) " " " 6.8 " " 7.3

again we find the same difficulty.

III. Boiling with an excess of H_2SO_4

(a) 10 cc. NH_4CNS Tube 4.5 Standard 7.3
(b) " " " 3 " " "

IV. Boiling with one acid or salt per 10 minutes.

(a) 10 cc. NH_4CNS Tube 7.4 Standard 7.3
(b) " " " 7.3 " " "
(c) " " " 7.2 " " "
(d) " " " 7.3 " " "

From the above results it is evident that you can not heat the cyanate to boiling in the presence of an acid or salt without danger of breaking it down.

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